

1.2 to 1.6 is at least 65 percent, more preferably 70 percent or more by number.

When the content of toner having shape coefficient of 1.0 to 1.6 is 65 number % or more, frictional charging characteristics by the developer carrying device is improved to be homogeneous, and accumulation of toner charged in access is prevented, cleaning of toner particles on photoreceptor is carried out effectively. Further, the generation of fine toner particles is inhibited since the toner particles are hard to be cracked, and therefore, the is easily carried out by employing cleaning device according to the present invention in combination.

Methods to control said shape coefficient are not particularly limited. For example, a method may be employed wherein a toner, in which the shape coefficient has been adjusted to the range of 1.2 to 1.6, is prepared employing a method in which toner particles are sprayed into a heated air current, a method in which toner particles are subjected to application of repeated mechanical forces employing impact in a gas phase, or a method in which a toner is added to a solvent which does not dissolve said toner and is then subjected to application of a revolving current, and the resultant toner is blended with a toner to obtain suitable

characteristics. Further, another preparation method may be employed in which, during the stage of preparing a so-called polymerization method toner, the entire shape is controlled and the toner, in which the shape coefficient has been adjusted to 1.0 to 1.6 or 1.2 to 1.6, is blended with a common toner.

Of the preparation methods, the polymerized toner method is preferable since it is simple as well as convenient as a toner production method, the surface uniformity is excellent compared to pulverized toner, and the like.

In order to uniformly control said shape coefficient of toner with minimal fluctuation of production lots, the optimal finishing time of processes may be determined while monitoring the properties of forming toner particles (colored particles) during processes of polymerization, fusion, and shape control of resinous particles (polymer particles).

Monitoring as described herein means that measurement devices are installed in-line, and process conditions are controlled based on measurement results. Namely, a shape measurement device, and the like, is installed in-line. For example, in a polymerization method, toner, which is formed employing association or fusion of resinous particles in water-based media, during processes such as fusion, the shape

as well as the particle diameters, is measured while sampling is successively carried out, and the reaction is terminated when the desired shape is obtained.

Monitoring methods are not particularly limited, but it is possible to use a flow system particle image analyzer FPIA-2000 (manufactured by Toa Iyodenshi Co.). Said analyzer is suitable because it is possible to monitor the shape upon carrying out image processing in real time, while passing through a sample composition. Namely, monitoring is always carried out while running said sample composition from the reaction location employing a pump and the like, and the shape and the like are measured. The reaction is terminated when the desired shape and the like is obtained.

The diameter of the toner particles of the present invention is preferably between 3 and 8 μm in terms of the number average particle diameter. When toner particles are formed employing a polymerization method, it is possible to control said particle diameter utilizing the concentration of coagulants, the added amount of organic solvents, the fusion time, or further the composition of the polymer itself.

By adjusting the number average particle diameter from 3 to 8 μm , it is possible to decrease the presence of toner

and the like which is adhered excessively to the developer conveying member or exhibits low adhesion, and thus stabilize developability over an extended period of time. At the same time, improved is the halftone image quality as well as general image quality of fine lines, dots, and the like.

The diameter of toner particles is designated as D (in μm). In a number based histogram, in which natural logarithm $\ln D$ is taken as the abscissa and said abscissa is divided into a plurality of classes at an interval of 0.23, a toner is preferred, which exhibits at least 70 percent of the sum (M) of the relative frequency (m_1) of toner particles included in the highest frequency class, and the relative frequency (m_2) of toner particles included in the second highest frequency class. By adjusting the sum (M) of the relative frequency (m_1) and the relative frequency (m_2) to at least 70 percent, the dispersion of the resultant toner particle size distribution narrows. Thus, by employing said toner in an image forming process, it is possible to securely minimize the generation of selective development.

In the present invention, the histogram, which shows said number based particle size distribution, is one in which natural logarithm $\ln D$ (wherein D represents the diameter of each toner particle) is divided into a plurality of classes

at an interval of 0.23 (0 to 0.23, 0.23 to 0.46, 0.46 to 0.69, 0.69 to 0.92, 0.92 to 1.15, 1.15 to 1.38, 1.38 to 1.61, 1.61 to 1.84, 1.84 to 2.07, 2.07 to 2.30, 2.30 to 2.53, 2.53 to 2.76...). Said histogram is drawn by a particle size distribution analyzing program in a computer through transferring to said computer via the I/O unit particle diameter data of a sample which are measured employing a Coulter Multisizer under the conditions described below.

Measurement Conditions

(1) Aperture: 100 μm

(2) Method for preparing samples: an appropriate amount of a surface active agent (a neutral detergent) is added while stirring in 50 to 100 ml of an electrolyte, ISOTON R-11 (manufactured by Coulter Scientific Japan Co.) and 10 to 20 ml of a sample to be measured is added to the resultant mixture. Preparation is then carried out by dispersing the resultant mixture for one minute employing an ultrasonic homogenizer.

The toner of the present invention may be prepared employing a method in which fine polymerization particles are prepared employing a suspension polymerization method, or a method in which monomers undergo emulsion polymerization in a solution to which an emulsified composition of necessary

additives is added, and thereafter, association is carried out by adding organic solvents, coagulants, and the like. During said association, listed are methods in which preparation is carried out in such a manner that a dispersion of releasing agents, colorants, and the like, which are required to constitute a toner, is mixed and association is carried out, emulsion polymerization is carried out upon dispersing toner components such as releasing agents, colorants, and the like into monomers, and the like. Said association as described herein denotes that a plurality of resin particles and colorant particles are allowed to fusing with each other.

In the invention, the "aqueous medium" is a medium containing at least 50% by weight of water.

Namely, various constitution materials such as colorants, and if desired, releasing agents, charge control agents, further polymerization initiators, and the like are incorporated into polymerizable monomers, and each of the constitution materials is dissolved in or dispersed into the polymerizable monomers employing a homogenizer, a sand mill, a sand grinder, an ultrasonic homogenizer, and the like. The polymerizable monomers, into which these various constitution materials are dissolved or dispersed, are dispersed into an

aqueous medium comprising a dispersion stabilizer so as to form oil droplets having a desired size. Thereafter, the resulting dispersion is transferred to a reaction apparatus having a stirring mechanism composed of stirring blades described below, and undergoes polymerization reaction upon raising its temperature. After completing the reaction, the dispersion stabilizer is removed, filtered, washed, and further dried to prepare the toner of the present invention.

The toner according to the invention can be also obtained by salting-off/coagulating resin particles prepared by the emulsion polymerization or the mini-emulsion polymerization. For example, the methods described in JP O.P.I. Nos. 5-265252, 6-329947 and 9-15904 are applicable.

The toner of the present invention is prepared employing a method in which a plurality of dispersion particles of the constitution materials comprised of resin particles, colorants and the like, or of fine particles comprised of resins, colorants, and the like, are associated, in which in particular, after dispersing these into water employing an emulsifier, the resulting dispersion is salted out by adding a coagulant in an amount of more than the critical coagulation concentration; at the same time, while forming fused particles upon heating the formed polymer at

least to the glass transition temperature of the polymer, so as to fuse with each other, the particle diameter is increased; when growing the particle diameter to a desired diameter, a large amount of water is added to halt the growth of the diameter; the particle surface is then smoothed through heating and stirring, whereby the shape is controlled; and the resulting particles are heat dried in a fluid state while suspended in a water comprising state. Further, herein, organic solvents which are infinitely soluble in water may be added at the same time, together with a coagulating agent.

Employed polymerizable monomers to constitute a resin include styrenes or styrene derivatives such as styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, α -methylstyrene, p-chlorostyrene, 3,4-dichlorostyrene, p-phenylstyrene, p-ethylstyrene, 2,4-dimethylstyrene, p-tert-butylstyrene, p-n-hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-decylstyrene, p-n-dodecylstyrene; methacrylic acid ester derivatives such as methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, n-octyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate, lauryl methacrylate,

phenyl methacrylate, diethylaminoethyl methacrylate, dimethylaminoethyl methacrylate, and the like; acrylic acid ester derivatives such as methyl acrylate, ethyl acrylate, isopropyl acrylate, n-butyl acrylate, t-butyl acrylate, isobutyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, stearyl acrylate, lauryl acrylate, phenyl acrylate, and the like; olefins such as ethylene, propylene, isobutylene, and the like; halogen based vinyls such as vinyl chloride, vinylidene chloride, vinyl bromide, vinyl fluoride, vinylidene fluoride, and the like; vinyl esters such as vinyl propionate, vinyl acetate, vinyl benzoate, and the like; vinyl ethers such as vinyl methyl ether, vinyl ethyl ether, and the like; vinyl ketones such as vinyl methyl ketone, vinyl ethyl ketone, vinyl hexyl ketone, and the like; N-vinyl compounds such as N-vinylcarbazole, N-vinylindole, N-vinylpyrrolidone, and the like; vinyl compounds such as vinyl naphthalene, vinylpyridine, and the like; acrylic acid or methacrylic acid derivatives such as acrylonitrile, methacrylonitrile, acrylamide and the like. These vinyl based monomers may be employed individually or in combination.

Further, still more preferably employed as polymerizable monomers, which constitute a resin, are those

having an ionic dissociation group in combination, which are, for example, have a substituent such as a carboxyl group, a sulfonic acid group, a phosphoric acid group, and the like as a group constituting the substituent. Listed as specific examples are acrylic acid, methacrylic acid, maleic acid, itaconic acid, cinnamic acid, fumaric acid, monoalkyl maleate, monoalkyl itaconate, styrenesulfonic acid, allylsulfosuccinic acid, 2-acrylamide-2-methylpropanesulfonic acid, acidphosoxyethyl methacrylate, 3-chloro-2-acidphophoxypropyl methacrylate, and the like.

Furthermore, the resin may be modified so as to have a cross-linking structure, employing multifunctional vinyls such as divinylbenzene, ethylene glycol dimethacrylate, ethylene glycol diacrylate, diethylene glycol dimethacrylate, diethylene glycol diacrylate, triethylene glycol dimethacrylate, triethylene glycol diacrylate, neopentyl glycol dimethacrylate, neopentyl glycol diacrylate, and the like.

These polymerizable monomers may undergo polymerization employing a radical polymerization initiator. In such cases, oil-soluble polymerization initiators may be employed in a suspension polymerization method. Such oil-soluble polymerization initiators include azo based or diazo based

polymerization initiators such as 2,2'-azobis-(2,4-dimethylvaleronitrile, 2,2'-azobisisobutyronitrile, 1,1'-azobis(cyclohexane-1-carbonitrile), 2,2'-azobis-4-methoxy-2,4-dimethylvaleronitrile, azobisisobutyronitrile, and the like; and peroxide based polymerization initiators and polymer initiators having a peroxide in the side chain such as benzoyl peroxide, methyl ethyl ketone peroxide, diisopropylperoxycarbonate, cumenehydroperoxide, t-butylhydroperoxide, di-t-butylperoxide, dicumylperoxide, 2,4-dichlorobenzoyloxide, lauroylperoxide, 2,2-bis-(4,4-t-butylperoxycyclohexyl)propane, tris-(t-butylperoxy)triazine, and the like.

Further, when the emulsion polymerization method is employed, water-soluble radical polymerization initiators may be employed. Water-soluble polymerization initiators include persulfates such as potassium persulfate, ammonium persulfate, and the like, azobisaminodipropene acetic acid salts, azobiscyanovaleric acid and salts thereof, hydrogen peroxide, and the like.

Listed as dispersion stabilizers may be tricalcium phosphate, magnesium phosphate, zinc phosphate, aluminum phosphate, calcium carbonate, magnesium sulfate, calcium hydroxide, magnesium hydroxide, aluminum hydroxide, calcium

metasilicate, calcium sulfate, barium sulfate, bentonite, silica, alumina, and the like. Further, also employed as dispersion stabilizers may be those which are generally employed as surface active agents such as polyvinyl alcohol, gelatin, methyl cellulose, sodium dodecylbenzenesulfonate, ethylene oxide adducts, higher alcohol sodium sulfate, and the like.

Preferred as excellent resins in the present invention are those having a glass transition point of 20 to 90 °C, as well as a softening point of 80 to 220 °C. The glass transition point is a value measured by a differential calorimetric method, while the softening point can be measured by an elevated type flow tester. Further, these resins preferably have a number average molecular weight (M_n) of 1,000 to 100,000, as well as a weight average molecular weight (M_w) of 2,000 to 1,000,000, which are measured by gel permeation chromatography. Further, as a molecular weight distribution, the M_w/M_n is preferably between 1.5 and 100, and is most preferably between 1.8 and 70.

The employed coagulating agents are not particularly limited, however those selected from metal salts are more suitable. Specific examples include salts of univalent

metals such as alkali metals, for example, sodium, potassium, lithium and the like; alkali earth metal salts of divalent metals such as calcium, magnesium, and the like; salts of divalent metals such as manganese, copper, and the like; and salts of trivalent metals such as iron, aluminum, and the like. Listed as specific salts can be sodium chloride, potassium chloride, lithium chloride, calcium chloride, zinc chloride, copper sulfate, magnesium sulfate, manganese sulfate, and the like. These may be employed in combination.

These coagulants are preferably added in an amount exceeding the critical coagulation concentration. The critical coagulation concentration as described herein is an index on the stability of an aqueous dispersion, and concentration at which coagulation is formed by the addition of a coagulant. The critical coagulation concentration varies greatly depending on the emulsified components and dispersing agents themselves. For example, the critical coagulation concentration is described in Seizo Okamoto, et al. "Kobunshi Kagaku (Polymer Chemistry)", edited by Nihon Kobunshi Gakkai, whereby detailed critical coagulation concentration data can be obtained. Furthermore, as another method, ζ (zeta) potentials of a specified particle dispersion are measured upon adding a desired salt to the

particle dispersion, while changing the salt concentration, and said salt concentration which varies the ζ potential can be obtained as the critical coagulation concentration.

The added amount of the coagulant of the present invention is acceptable if it exceeds the critical coagulation concentration. However, the addition amount is preferably at least 1.2 times of the critical coagulation concentration, and is more preferably at least 1.5 times.

A solvent which is infinitely soluble denotes a solvent which is infinitely soluble in water and as such solvents, those which do not dissolve the resin formed in the present invention are selected. Specifically, cited are alcohols such as methanol, ethanol, propanol, isopropanol, t-butanol, methoxyethanol, butoxyethanol, and the like, nitriles such as acetonitrile, and ethers such as dioxane. In particular, ethanol, propanol and isopropanol are preferred.

The added amount of such solvents which are infinitely soluble is preferably between 1 and 100 percent by volume of the polymer containing dispersion to which the coagulant is added.

Further, in order to make all particles of a uniform shape, after preparing colored particles and filtering them, the resulting slurry, in which water is present in an amount

of at least 10 percent by weight of the particles, is preferably subjected to fluidized drying. At the time, those which comprise a polar group in the polymer are particularly preferred. As the reason, it is assumed that since existing water somewhat exhibits swelling effect for the polymer comprising the polar group, making particles of a uniform shape tends to be particularly easily carried out.

The toner of the present invention comprises at least a resin and a colorant, but may as well comprise a releasing agent which works as a fixing property improving agent, a charge control agent, and the like. Further, external additives comprised of fine inorganic particles, fine organic particles, and the like may be added to toner particles which are mainly comprised of the above-mentioned resin and colorant.

Optionally employed as colorants, which are employed in the toner of the present invention, may be carbon blacks, magnetic materials, dyes, pigments, and the like. Employed as said carbon blacks are channel black, furnace black, acetylene black, thermal black, lamp black, and the like. Employed as magnetic materials may be ferromagnetic metals such as iron, nickel, cobalt, and the like, as well as alloys which do not comprise ferromagnetic metals and are subjected

to thermal treatment to exhibit ferromagnetism, such types of alloys being called Heusler alloys, being for example, manganese-copper-aluminum, manganese-copper-tin and the like, and also chromium dioxide, and the like.

Employed as dyes can be C.I. Solvent Red 1, Solvent Red 49, Solvent Red 52, Solvent Red 58, Solvent Red 63, Solvent Red 111, and Solvent Red 122, C.I. Solvent Yellow 19, Solvent Yellow 44, Solvent Yellow 77, Solvent Yellow 79, Solvent Yellow 81, Solvent Yellow 82, Solvent Yellow 93, Solvent Yellow 98, Solvent Yellow 103, Solvent Yellow 104, Solvent Yellow 112, and Solvent Yellow 162; C.I. Solvent Blue 25, Solvent Blue 36, Solvent Blue 60, Solvent Blue 70, Solvent Blue 93, and Solvent Blue 95, and the like. Furthermore, these mixtures may be employed. Employed as pigments may be C.I. Pigment Red 5, Pigment Red 48:1, Pigment Red 53:1, Pigment Red 57:1, Pigment Red 122, Pigment Red 139, Pigment Red 144, Pigment Red 149, Pigment Red 166, Pigment Red 177, Pigment Red 178, and Pigment Red 222; C.I. Pigment Orange 31, and Pigment Orange 43; C.I. Pigment Yellow 14, Pigment Yellow 17, Pigment Yellow 93, Pigment Yellow 94, and Pigment Yellow 138; and C.I. Pigment Green 7; and C.I. Pigment Blue 15:3, and Pigment Blue 60; and the like. These mixtures may also be employed. The average primary particle diameter varies

depending on type, generally, however it is preferably between about 10 and about 200 nm.

The colorants may be added by a methods, in which colorants are added during which polymer particles prepared by an emulsion polymerization method are coagulated by adding a coagulant and the polymer is tinted; during polymerizing of said monomers, a colorant is added and the resulting mixture is polymerized to form tinted particles; and the like. Further, when the colorant is added during polymer preparation, it is preferably subjected to surface treatment employing a coupling agent and the like, which is employed so that radical polymerization is not hindered.

Further, added as fixing property enhancing agents may be low molecular weight polypropylene (having a number average molecular weight of 1,500 to 9,000) or low molecular weight polyethylene.

Charge control agents may also be employed, which are known in the art, and can be dispersed into water.

Specifically listed are Nigrosine based dyes, metal salts of naphthenic acid or higher fatty acids, alkoxylated amines, quaternary ammonium salts, azo based metal complexes, salicylic acid metal salts or metal complexes thereof, and such. Further, these charge control agents and fixing

property enhancing agents are preferably in a dispersed state, and the number average primary particle diameter is adjusted from about 10 to about 500 nm.

In a suspension polymerization method in which a composition, prepared by dispersing or dissolving toner constitution components such as a colorant and the like in polymerizable monomers, is suspended in a water based medium, and then undergoes polymerization to obtain the toner, the shape of toner particles may be controlled by controlling the flow of the medium in a reaction vessel in which the reaction is carried out. Namely, when many toner particles having a shape coefficient of at least 1.2 are formed, the flow in the reaction vessel is regulated to a turbulent one; polymerization proceeds; and when oil droplets suspended in the water based medium are gradually polymerized and oil droplets become soft particles, particle union is accelerated due to collisions of particles resulting in particles which are not stable in shape. Further, when spherical toner particles having a shape coefficient of not more than 1.2 are formed, the flow of the medium in said reaction vessel is regulated to a laminar flow to result in spherical particles upon minimal collisions between particles. Employing such methods, it is possible to control the toner shape

distribution within the range specified by the present invention.

In the suspension polymerization, said turbulent flow may be generated employing specified stirring blades, and the shape may be readily controlled.

On the other hand, for a toner prepared by a polymerization method in which resin particles are associated or fused in an aqueous medium, it is possible to optionally vary the shape distribution as well as the shape of the particles by controlling the flow of a medium and the temperature distribution in the reaction vessel during the fusing stage, and further by controlling the heating temperature, the rotational frequency while stirring, and the time during the shape controlling process, after fusing.

Regarding the toner prepared by the polymerization method in which resin particles are associated or fused, it is possible to prepare a toner, having specific shape coefficient and the uniform shape distribution described in the present invention, by controlling the temperature, the rotation frequency and the time during the fusing process and shape controlling process, employing stirring blades as well as a stirring vessel which is capable of making the flow in the reaction vessel a laminar flow and the interior

temperature distribution uniform. As the reason, it is assumed that when fusing is carried out in the location in which the laminar flow is generated, particles (associated or coagulated particles) while undergoing coagulation and fusing are not subjected to strong stress, and in the laminar flow in which the flow rate is accelerated, the temperature distribution in the stirring vessel is uniform, and as a result, the shape distribution of fused particles becomes uniform. Further, the fused particles are gradually varied to spherical particles by heating and stirring in the subsequent shape controlling process, and the shape of toner particles may thus be optionally controlled.

Blades and a stirring vessel, which are employed to prepare a toner employing the polymerization method in which resin particles are associated or fused, may be employed which are similar to those which are employed to generate a laminar flow in the above-mentioned suspension polymerization method. The stirring blades are preferably constituted at several levels in such a manner that the upper stirring blade is arranged so as to make an advanced crossed axes angle α in the rotational direction with respect to the lower stirring blade in the same manner as the case of the stirring

blades which are employed for the above-mentioned suspension polymerization method.

Furthermore, the toner of the present invention may be advantageously employed when combined with external additives of fine particles, such as fine inorganic particles and fine organic particles. As the reason for such combining, it is assumed that burying and releasing of external additives may be effectively minimized, and its effect is markedly exhibited.

Preferably employed as such fine inorganic particles are inorganic oxide particles such as silica, titania, alumina, and the like. These fine inorganic particles are preferably subjected to hydrophobic treatment employing silan coupling agents, titanium coupling agents, and the like. The degree of the hydrophobic treatment is not particularly limited, however the degree is preferably between 40 and 95 measured as methanol wettability. The methanol wettability as described herein means the evaluation of wettability for methanol. In this method, 0.2 g of fine inorganic particles is weighed and added to 50 ml of distilled water placed in a 200 ml beaker. Methanol is slowly added dropwise while slowly stirring from a burette of which top is immersed in the solution until entire fine organic particles are wet.

The degree of hydrophobicity is calculated from the formula given below:

$$\text{Degree of hydrophobicity} = a / (a + 50) \times 100$$

wherein "a" (in ml) represents the amount of methanol required for making fine inorganic particles perfectly wet.

The added amount of said external additives is between 0.1 and 5.0 percent by weight of the toner, and is preferably between 0.5 and 4.0 percent by weight. As external additives, various materials may be employed in combination.

The toner according to the invention may be employed for a two-component developer, non-magnetic single component developer or magnetic single component developer, and is employed for the two-component developer most suitably.

A coated carrier composed of styrene-acryl resin, fluorinated acryl resin or silicon resin coated on iron powder, ferrite core or magnetite core is preferably employed as a carrier when the toner for developing static latent image according to the invention is employed in the two-component developer.

Further, even in the case in which a reversal development system is employed which has resulted in marked problems such as insufficient cleaning, when used in the conventional cleaning unit, the present invention is

effectively employed since desired cleaning effects are assured.

The preferable embodiments of the invention are described.

1. An image forming apparatus, described above, wherein said toner employed for image visualization comprises at least 65 percent of toner particles in the range of shape coefficient of 1.0 to 1.6.
2. An image forming apparatus, described above, wherein said toner employed for visualization has a number average particle diameter in the range of 3 to 8 μm .
3. An image forming apparatus, described above, wherein said toner employed for visualization is comprised of toner particles which are formed by polymerizing a polymerizable monomer in a water based medium.
4. An image forming apparatus, described above, wherein toner particles are formed by coalescing toner particles which have been formed by polymerizing a polymerizable monomer in a water based medium.
5. In an image forming method comprising a development process which visualizes a latent image formed on an photoreceptor, employing a toner, and a cleaning process which removes any residual toner on said photoreceptor after

transferring a toner image on said photoreceptor onto a transfer material, an image forming method wherein said cleaning process comprises two cleaning members consisting of a first cleaning member and a second cleaning member upstream along the conveyance direction of said photoreceptor, and at least 50 percent of the residual toner is removed by said first cleaning member and any residual toner is removed by said second cleaning member.

EXAMPLES

Specific examples of the present invention will now be described.

<Example 1-1>

According to the constitution of the image forming apparatus shown in Fig. 1(a), the photoreceptor, development unit, the toner, the cleaning roller, and the cleaning blade were set as described below.

(1) Photoreceptor

Employed as photoreceptor 10, was a drum-shaped organic photoreceptor which was prepared by forming a 25 μm thick photosensitive layer comprised of polycarbonate comprising phthalocyanine pigments on the circumferential surface of a drum-shaped aluminum base body. The friction coefficient

between the surface of photoreceptor (10) and the used cleaning blade was 1.2

(2) Development Unit

Employed as development unit 13 was a unit fitted with rotationally-driven development sleeve 13A at a linear speed of 370 mm/minute, to which a bias voltage having the same polarity as the surface potential of photoreceptor 10 was applied so that reversal development was carried out employing a two-component developer.

The toner constituting said two-component developer was comprised of toner particles having a volume average particle diameter of $6.5\text{ }\mu\text{m}$ and a negative polarity, prepared by employing an emulsion polymerization.

(3) Cleaning Roller

Employed as cleaning roller 21 was a roller having a surface resistance of $10^4\text{ }\Omega\text{cm}$, comprised of conductive foamed urethane.

Said cleaning roller 21 was rotationally driven so as to move the contact portion with photoreceptor 10 in the same direction as said photoreceptor 10, and the linear speed ratio V_r/V_p of the linear speed V_r of cleaning roller 21 to the linear speed V_p of photoreceptor 10 was set at 1.

(4) Cleaning Blade

Employed as cleaning blade 23 was a blade comprised of urethane rubber, having a repulsion elasticity modulus of 50 percent (at 25 °C), a JIS A Hardness of 70 degrees, a thickness of 2.00 mm, a free length of 10 mm, and a width of 324 mm.

Further, cleaning blade 23 was arranged so that contact angle θ_1 and fulcrum angle θ_2 were 23 degrees and 20 degrees, respectively ($\theta_1 > \theta_2$). Pressing means 27 was set to result in a contact load of 20 g/cm to photoreceptor 10, employing a 350 g weight.

Under the above conditions, surface potential V_h of the unexposed area of photoreceptor 10 was set at -750 V and surface potential V_l of the exposed area of photoreceptor 10 was set at -100 V. Further, a -600 V development bias was applied to development sleeve 13A.

Further, by applying +20 μ A to cleaning roller 21 employing bias voltage applying means 22 comprised of a constant current power source, said cleaning roller 21 was charged so that the surface potential reached +600 V.

Employing the image forming apparatus as above, practical imaging tests were carried out via printing 200,000

sheets, and blade curl-under as well as minute vibrations were evaluated. In said practical imaging test, printing of the 1st to the 100,000th sheet was carried out at high temperature and high humidity (at 30 °C and 80 percent relative humidity), printing of the 100,001st to the 150,000th sheet at normal temperature and normal humidity (20 °C and 50 percent relative humidity) and printing of the 150,001st to the 200,000th sheet was carried out at low temperature and low humidity (10 °C and 20 percent relative humidity). Table 1-1 lists the results.

<Comparative Examples 1-1 through 1-3>

Practical imaging tests were carried out in the same manner as Example 1-1, except that contact conditions of cleaning blade 23 to photoreceptor 10 were varied according to Table 1-1 below. Table 1-1 shows the results.

Table 1-1

	Contact Angle 01	Fulcrum 02	Image Staining		Remarks
			Blade Curl- Under	Minute Vibrations	
Example 1-1	23°	20°	good to the 200,000th sheet	good to 200,000th sheet	good to the 200,000th sheet
Comparative Example 1-1	20°	23°	occurred at about the 120,000th sheet	continually occurred after the 100,000th sheet	the test was terminated at the 120,000th sheet
Comparative Example 1-2	0°	-5°	-	-	the test was terminated at the 10,000th sheet
Comparative Example 1-3	35°	32°	occurred at about the 140,000th sheet	continually occurred after the 120,000th sheet	the test was terminated at the 140,000th sheet

As noted, it was confirmed that when the image forming apparatus of the present invention according to Example 1-1 was employed, it was possible to form high quality images over an extended period of time without effects of ambience.

<Example 1-2>

An image forming apparatus was constituted in the same manner as Example 1-1 except that cleaning blade 23 was

disposed so as to form contact angle θ_1 of 10 degrees and fulcrum angle θ_2 of 12 degrees ($\theta_1 < \theta_2$), and a control mechanism to carry out a specified toner image forming process was provided. In the resultant image forming apparatus, by controlling the action of exposure unit 12, employing said control mechanism, said specified toner image having a width of 320 mm and circumferential direction length of 1 mm was formed and when said specified toner image passed through the cleaning zone employing cleaning roller 21, the roller effect decreasing function which eliminated the bias voltage applied to cleaning roller 21 was simultaneously allowed to function. Further, it was set so that said specified toner image was formed at the beginning of the practical imaging test, thereafter was adjusted based on the total number of copied sheets and the atmospheric ambience so that said specified toner images were formed at the frequency shown in the table below, and also formed at the completion of the practical imaging test.

Employing said image forming apparatus, practical imaging was carried out via printing 200,000 sheets, and the presence and absence of blade curl-under and image staining was evaluated. Table 1-3 shows the results.

In said practical imaging test, printing of the 1st to the 100,000th sheet was carried out at high temperature and high humidity (at 30 °C and 80 percent relative humidity), printing of the 100,001st to the 150,000th sheet at normal temperature and normal humidity (20 °C and 50 percent relative humidity) and printing of 150,001st to 200,000th sheet was carried out at low temperature and low humidity (10 °C and 20 percent relative humidity).

<Example 1-4>

A practical imaging test was carried out in the same manner as Example 1-2, except that the specified toner image forming function and the roller effect decreasing function in the control mechanism were not completely operated. Table 1-3 shows the results.

<Comparative Example 1-5>

Practical imaging tests were carried out in the same manner as Example 1-2, except that the roller effect decreasing function was not allowed to operate. Table 1-3 shows the results.

Table 1-2

Operation Ambience	Total Number of Copy Sheets	Frequency of Specified Toner Image Formation
Ambience at High Temperature and High Humidity	1 to 100,000 sheets	once per 5 sheets
Ambience at Normal Temperature and Normal Humidity	100,001 to 150,000 sheets	once per 50 sheets
Ambience at Low Temperature and Low Humidity	150,001 to 200,000 sheets	once per 50 sheets

Table 1-3

	Operation of Specified Toner Image Forming Function	Operation of Roller Effect Decreasing Function	Evaluation
Example 1-2	used	used	good to the 200,000th sheet
Comparative Example 1-4	not used	not used	blade curl-under occurred at about the 30,000th sheet and the test was terminated
Comparative Example 1-5	used	not used	blade curl-under occurred at about the 80,000th sheet and the test was terminated

As noted, it was confirmed that the image forming apparatus of the present invention according to Example 1-2 was capable of carrying out stable production of high quality images irrespective of ambient effects, over an extended

period of time. Further, since the specified toner image was formed at the completion of the practical imaging test, it was capable of sufficiently exhibiting cleaning effects employing the cleaning blade, even in use after the completion of the test.

In the foregoing, the embodiments of the present invention were described.

(1) The frequency of the specified toner image formation may be set based on, for example, time employed for image formation.

(2) The roller effect decreasing function in said control mechanism may be controlled so that the magnitude of the bias voltage applied to the cleaning roller is smaller than common cleaning process.

(3) Toner employed in the present invention may be employed in either a one-component developer or a two-component developer. Further, said toner may be employed as either a magnetic toner or a non-magnetic toner.

Further, the development system of latent images is not limited to the reversal development method.

In the image forming apparatus of the present invention, in addition to electrostatic cleaning obtained by employing the cleaning roller, mechanical cleaning employing

a cleaning blade is carried out. As a result, highly effective cleaning is exhibited, and it is possible to assuredly remove residual toner. Furthermore, the position of rotationally driven center axis O is set so that the state of the cleaning blade satisfies the specified conditions. As a result, the load, which is applied to the leading edge of the cleaning blade while the photoreceptor is rotationally driven, acts so as to rotate the cleaning blade in the direction to allow the cleaning blade to separate from the surface of the photoreceptor, utilizing rotationally driven center axis O as the center. Therefore, it is possible to minimize the formation of blade curl-under as well as minute vibrations. At the same time, it is possible to obtain desired residual toner removing ability. Consequently, it is possible to carry out stable production of high quality images over an extended period of time.

Further, in the image forming apparatus in the present invention, by allowing the cleaning blade to remove toner images for maintaining blade effects, which are formed on the photoreceptor, lubricating action is effected between the cleaning blade and the photoreceptor, employing toner comprising lubricants as the external agent which constitutes toner images for maintaining said blade effects. As a

result, it is possible to retard friction force acted on the leading edge of the cleaning blade to become excessive and to minimize the formation of blade curl-under as well as minute vibrations. Accordingly, it is possible to carry out stable production of high quality images over an extended period of time.

<Example 2-1>

According to the constitution of the image forming apparatus shown in Fig. 1(b), the photoreceptor, the development unit, the toner, the cleaning roller, and the cleaning blade were installed as described below.

(1) Photoreceptor

Employed as photoreceptor 10, was a drum-shaped organic photoreceptor which was prepared by forming a 25 μm thick photosensitive layer comprised of polycarbonate comprising phthalocyanine pigments on the circumferential surface of a drum-shaped aluminum base body.

(2) Charging Unit

As charging unit 11 was a scorotron charging unit. The effective charging area W3 of said charging unit was 318 mm.

(3) Development Unit

Employed as development unit 13 was a unit fitted with rotationally driven development sleeve 13A, to which a bias

voltage having the same polarity as the surface potential of photoreceptor 10 was applied so that reversal development was carried out employing a two-component developer.

The toner constituting said two-component developer was comprised of toner particles having a volume average particle diameter of 6.5 μm , prepared employing an emulsion polymerization and had a negative polarity.

(4) Cleaning Roller

Employed as cleaning roller 21 was a roller having a surface resistance of $10^4 \Omega\text{cm}$, comprised of conductive foamed urethane. The effective cleaning area W1 of said cleaning roller 21 was 320 mm.

Said cleaning roller 21 was rotationally driven so as to move the contact portion with photoreceptor 10 in the same direction as said photoreceptor 10, and the linear speed ratio V_r/V_p of the linear speed V_r of cleaning roller 21 to the linear speed V_p of photoreceptor 10 was set at 1.1.

(5) Cleaning Blade

Employed as cleaning blade 23 was a blade comprised of urethane rubber, having a JIS A Hardness of 70 degrees, a thickness of 2.00 mm, and a free length of 10 mm.

Further, contact angle θ and contact load to photoreceptor 10 were set at 10 degrees and 20 g/cm, respectively.

(6) Other

Employed as transfer unit 14 was a corona discharge unit having effective transfer area W3 of 300 mm.

Under the above conditions, surface potential V_h of the unexposed area of photoreceptor 10 was set at -750 V and surface potential V_l of the exposed area of photoreceptor 10 was set at -100 V. Further, of -600 V development bias was applied to development sleeve 13A.

Further, by applying +20 μA to cleaning roller 21 employing bias voltage applying means 22, comprised of a constant current power source, said cleaning roller 21 was charged so that the surface potential reached +600 V.

Employing the image forming apparatus as above, practical imaging tests were carried out by printing the 200,000 sheets, and interior apparatus staining as well as insufficient cleaning was evaluated. In said practical imaging test, printing of the 1st to the 100,000th sheet was carried out at normal temperature and normal humidity (20 °C and 50 percent relative humidity) and printing of the

100,001st to the 200,000th sheet was carried out at high temperature and high humidity (at 30 °C and 80 percent relative humidity). Table 2-1 shows the results.

<Comparative Examples 2-1 through 2-3>

Practical imaging was carried out in the same manner as Example 2-1, except that W1, W2, and W3 were varied based on Table 2-1. Table 2-1 shows the results.

Table 2-1

	W1 (in mm)	W2 (in mm)	W3 (in mm)	Interior Apparatus Staining	Insuffi- cient Cleaning	Remarks
Example 2-1	320	300	318	good to the 200,000th sheet	good to the 200,000th sheet	good to the 200,000th copy
Comparative Example 2-1	300	320	268	occurred at about the 50,000th sheet	occurred at about the 100,000th sheet	the test was termi-nated at the 100,000th copy due to insuffi- cient cleaning
Comparative Example 2-2	320	300	268	occurred around the 100,000th sheet	occurred at about the 80,000th sheet	great interior apparatus staining
Comparative Example 2-3	320	330	318	occurred at about the 160,000th sheet	good to the 200,000th sheet	great interior apparatus staining

As noted above, it was confirmed that the image forming apparatus of the present invention, employed in Example 2-1, resulted in no interior apparatus staining and was capable of producing high quality images over an extended period of time. Contrary to this, it was confirmed that the image forming apparatuses employed in Comparative Examples 2-1 through 2-3 were not commercially viable because all resulted in interior apparatus staining, and the apparatuses employed in Comparative Examples 2-1 and 2-2 resulted in belt-shaped insufficient cleaning.

<Example 2-2>

An image forming apparatus was constituted in the same manner as Example 2-1, except that cleaning roller 30 was employed in which insulated part 32 beyond both ends of conductive part 31 corresponding to effective charging area W3 of charging unit 11 was formed to be 10 mm for each end, and effective charging area W3 of charging unit 11 was set at 302 mm. Employing said apparatus, practical imaging tests, in which 200,000 sheets were printed, were carried out under conditions described below and interior apparatus staining as well as insufficient cleaning was evaluated. As a result, it was confirmed that said apparatus resulted in neither

interior apparatus staining nor insufficient cleaning and produced high quality images over an extended period of time.

Said imaging tests were carried out at the ambient conditions described below:

from the first to the 100,000th sheet at normal temperature and normal humidity (20 °C and 50 percent relative humidity);
from the 100,001st to the 150,000th sheet at low temperature and low humidity (10 °C and 20 percent relative humidity);
from the 150,001st to the 200,000th sheet at high temperature and high humidity (30 °C and 80 percent relative humidity).

The embodiments of the present invention were described above. However, the present invention is not limited to the aforesaid embodiments.

(1) Said charging unit may be either of a non-contact type or a contact type. For example, it may be comprised of a roller to which a voltage can be applied. In this case, the effective charging area is the actual width which comes into contact with the photoreceptor surface.

(2) As the cleaning blade holding system in said cleaning unit, it is possible to employ a rotary type blade holder which is rotatable around the axis in parallel to the rotational axis of the photoreceptor and provides a definite

contact pressing force to a cleaning blade utilizing a spring or gravity load.

(3) It is possible to employ rollers and brushes other than said scraper to remove toner which has been transferred from said cleaning roller.

(4) The toner employed in the present invention may be used in either one component developer or two-component developer, and may be either a magnetic toner or a non-magnetic toner.

Further, latent image development systems are not limited to the reversal development method.

(5) It is possible to apply various constitutions to the insulated part of the cleaning roller. For example, a whole roller may be constituted employing the same conductive/semi-conductive materials and may be constituted so that the part located beyond both ends of the part corresponding to the effective charging area obtained by the charging unit is covered with an insulating coating or tube.

In the image forming apparatus of the present invention, in addition to mechanical cleaning, employing a cleaning blade, electrostatic cleaning, employing a cleaning roller, is carried out. As a result, since basically high cleaning effects are exhibited, it is possible to assuredly remove residual toner on the image holding body. In

addition, since effective cleaning area W1 obtained by the cleaning roller is set in the specified range, it is possible to allow the removal electric field formed between the photoreceptor and the cleaning roller to act on the specified area in the axis direction of said photoreceptor. As a result, it is possible to assuredly minimize interior apparatus staining due to toner adhesion as well as insufficient cleaning due to dielectric breakdown of the photosensitive layer of the photoreceptor, and to stably produce high quality images over an extended period of time.

Further, in the image forming apparatus of the present invention, due to the fact that the bias voltage applying means is a constant current power source, electric potential difference between the surface of the cleaning roller and the surface of the photoreceptor is formed so as to run electric current at a constant amount, and said electric potential difference is simultaneously adjusted so as to keep constant irrespective of the variation of the surface potential of the photoreceptor. As a result, it is possible to more assuredly minimize unevenness and insufficient cleaning due to the electric potential level and polarity of the photoreceptor, compared to the case in which a constant voltage power source is employed.

Still further, in the image forming apparatus of the present invention, the portion beyond both ends of the part corresponding to the effective charging area in the lateral direction of the cleaning roller is insulated. Since the opposite charge area, which is charged employing the cleaning roller and is not recharged employing the charging unit, is not formed on the surface of the photoreceptor, neither interior apparatus staining due to toner adhesion, nor insufficient cleaning due to dielectric breakdown of the photosensitive layer is formed. As a result, it is possible to maintain high cleaning performance over an extended period of time and to produce high quality images.

Further, insulting portions are formed on the cleaning roller. As a result, it is possible to assuredly minimize the problem in which toner, which has been recovered, is scattered on the side of the photoreceptor and re-adheres onto the photoreceptor.

In the cleaning unit of the present invention, the parts beyond both ends of the part, corresponding to the charging area of the photoreceptor, are insulated in the lateral direction of the cleaning roller. As a result, since the area beyond the effective charging area of the photoreceptor is not charged by the cleaning roller, neither

interior apparatus staining due to toner adhesion nor insufficient cleaning due to dielectric breakdown of the photoreceptor occurs. As a result, it is possible to exhibit uniform cleaning effects over an extended period of time.

Example 3

In the examples described in Fig. 1(b), images were formed employing an image forming apparatus comprised of units carrying out each process of exposure, development, transfer, fixing, and cleaning.

Further, employed as the present photoreceptor was a negatively chargeable OPC photoreceptor. Negatively charged electrostatic latent images were formed on said photoreceptor and toner images were formed on said photoreceptor via reversal development utilizing a negatively charged toner.

The linear speed of the present photoreceptor was 370 mm/second. Further, a negatively chargeable toner of a volume average particle diameter of 6.5 μm was employed.

[A] Example of Embodiment 1

(1) Example A-1

i) Photoreceptor

The present photoreceptor A-1 was prepared as described below.

<Interlayer>

Titanium chelate compound (TC-750,
manufactured by Matsumoto Seiyaku) 30 g
Silane coupling agent (KBM05-3,
manufactured by Shin-Etsu Kagaku Co.) 17 g
2-Propanol 150 ml

Said interlayer was applied so as to obtain a dried layer thickness of 0.5 mm onto an aluminum drum base body which had been machined to obtain a raw tube surface roughness of 1.4 μm .

<Charge Generating Layer>

Y type titanyl phthalocyanine 60 g
Silicone-modified butyral resin (X-40-1211,
manufactured by Shin-Etsu Kagaku Co.) 700 g
2-Butanone 2000 ml

were blended and dispersed for 10 hours employing a sand mill, whereby a charge generating layer coating composition was prepared. Said coating composition was applied onto said interlayer, employing a dip coating method, whereby a charge generating layer, having a dried layer thickness of 0.2 μm , was prepared.

<Charge Transport Layer>

Charge transport material (4-methoxy-4'-

(4-methyl- α -phenylstyryl)triphenylamine)	200 g
Polycarbonate (TS2050, manufactured by Teijin Kasei Co.)	300 g
Dichloromethane	2000 ml

were blended and dissolved, whereby a charge transport coating composition was prepared. The resulting coating composition was applied onto said charge generating layer, employing a dip coating method to prepare a charge transport layer, having a dried layer thickness of 20 μm , whereby Present Photoreceptor A-1 was prepared.

(2) Example A-2

Present Photoreceptor A-2 was prepared as described below.

Present Photoreceptor A-2 was prepared in the same manner as Present Photoreceptor A-1, except that the raw tube surface roughness of the aluminum drum of Example A-1 was machined so as to result in 0.3 μm .

(3) Example A-3

Present Photoreceptor A-3 was prepared as described below.

An interlayer, a charge generating layer and a charge transport layer were prepared in the same manner as said Present Photoreceptor A-1.

<Resinous Layer>

Methyltrimethoxysilane	150 g
Phenyltrimethoxysilane	30 g
Antioxidant (Exemplified Compound 1-8)	1 g
2-propnol	225 g
2 percent Acetic acid	106 g
Tris(acetylacetonato)aluminum	4 g
Colloidal silica (30 percent methanol dispersion, manufactured by Nissan Kagaku Co.)	103 g

were blended to prepare the coating composition of a resinous layer. The resulting coating composition was applied onto said charge transport layer so as to obtain a resinous layer having a dried layer thickness of 2.5 μm , employing a circular amount regulating type coating apparatus. The resulting coating was then heated and hardened at 110 °C for one hour, whereby a siloxane based resinous layer having a cross-linked structure was formed. Thus Present Photoreceptor A-3 was prepared.

(4) Comparative Example A-1

Comparative Example A-1 was prepared as described below.

Comparative Example A-1 was prepared in the same manner as Present Photoreceptor A-1, except that the aluminum base body employed to prepare Present Photoreceptor A-1 was subjected to mirror grinding.

(5) Comparative Example A-2

Comparative Photoreceptor A-2 was prepared in the same manner as Present Photoreceptor A-1 except that an aluminum drum base body was employed which had been machined to result in a raw tube surface roughness of 2.5 μm .

Surface roughness R_z of Present Photoreceptors A-1 through A-3 and Comparative Photoreceptors A-1 and A-2 was determined employing a surface roughness meter (Surfcorder SE-30H, manufactured by Kosaka Kenkyusho Co.). Measurement conditions as well as measurement results are described below.

Measurement Conditions

Measurement rate: 0.1 mm/second

Measurement distance: 15 mm

Trace: 2 μm

Measurement Results

	Surface Roughness Rz (in μm)
Present Photoreceptor A-1	1.80
Present Photoreceptor A-2	0.35
Present Photoreceptor A-3	2.40
Comparative Photoreceptor A-1	0.05
Comparative Photoreceptor A-2	2.80

ii) Cleaning Roller

The cleaning roller was comprised of conductive foamed urethane, and was comprised of an elastic roller having a surface resistivity of $10^3 \Omega/\square$ and a hardness of 30 degrees. Said roller was prepared by winding urethane onto a $\Phi 6$ mm metal shaft so as to form $\Phi 16$ mm (having a thickness of 25 mm) and was brought into contact with said photoreceptor to result in a contact width of 2 mm.

Said roller moved in the normal direction to said photoreceptor in the contact area at a circumferential speed ratio of 1 : 1.

iii) Bias Voltage

A current at 20 μA and a positive bias voltage were applied to said cleaning roller employing a constant current power source.

iv) Removal Means

A scraper made of SUS was brought into contact with said cleaning roller utilizing a counter system.

v) Cleaning Blade

A cleaning blade comprised of urethane rubber, having a thickness of 2.0 mm, a free length of 10 mm, and a hardness of 70 degrees, was brought into contact with said photoreceptor at a contact angle of 15 degrees, utilizing a counter system. The contact load was 20 g/cm.

vi) Developer

A two-component developer comprised of a toner and a carrier was employed. Said toner, having a volume average particle diameter of 6.5 μm , was prepared employing a granulation polymerization method.

Image formation experiments, employing 200,000 sheets, were carried out under the conditions previously described and the ambient conditions described below. The following results were obtained.

a. High temperature and high humidity from the first to the 100,000th sheet (30 °C and 80 percent relative humidity)

b. Normal temperature and normal humidity from the 100,001st to the 200,000th sheet (20 °c and 50 percent relative humidity)

i) Examples A-1 through A-3 resulted in no blade curl-under and produced high quality images during image formation of all 200,000 sheets.

ii) Comparative Example A-1 resulted in curl-under at a very early stage (image formation of 10,000 sheets), and image forming experiments had to be terminated.

iii) Comparative Example A-2 produced excellent images until the image formation of the 130,000th sheet in the same manner as examples. However, after the image formation of the 130,001st sheet, insufficient cleaning occurred due to abrasive wear of the cleaning blade, whereby black streaks and white streaks were formed on images. Said problems were more pronounced as the image formation proceeded, and the image formation was terminated at the 150,000th sheet.

[B] Example of Embodiment 2

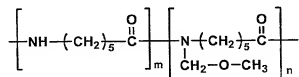
i) Photoreceptor

(1) Example B-1

Photoreceptor (hereinafter referred to as Present Photoreceptor) B-1 according to the present embodiment was prepared as described below.

After dispersing a mixture consisting of 10 weight parts of conductive titanium oxide (coated with tin oxide, having an average primary particle diameter of 0.4 μm), 10 weight parts of a phenol resin precursor (being a resol type), 10 weight parts of methanol, and 10 weight parts of butanol, employing a sand mill, the resulting dispersion was dip-coated onto an aluminum cylinder. After hardening the resulting coating at 140 $^{\circ}\text{C}$, a conductive layer having a volume resistivity of $5 \times 10^9 \Omega\text{cm}$ and a thickness of 20 μm was provided.

Subsequently, 10 weight parts of methoxymethylated nylon (at a ratio of methoxymethylation of about 30 percent) having the structural formula described below

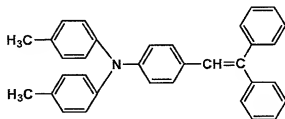


and 150 weight parts of isopropanol were mixed and dissolved. Thereafter, the resulting composition was applied onto said conductive layer, whereby a 1 μm thick sublayer was provided.

Subsequently, a mixture consisting of 4 weight parts of TiOPc having strong peaks at 9.5 degrees and 27.1 degrees at a diffraction angle of $2\theta \pm 0.2$ degrees of X-ray diffraction

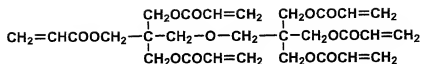
spectra of CuK α , 2 weight parts of polyvinyl butyral (having the trade name of Eslex BM2, manufactured by Shin-Etsu Kagaku), and 60 weight parts of methyl ethyl ketone were dispersed for 4 hours in a sand mill employing Φ 1 mm glass beads, whereby a charge generating layer dispersion was prepared. The resulting dispersion was dip-coated and a 0.3 μ m thick charge generating layer was provided.

Then, a mixture consisting of 10 weight parts of triphenylamine having the structural formula described below,



10 weight parts of a polycarbonate resin (Bisphenol Z, having a viscosity average molecular weight of 20,000), 50 weight parts of monochlorobenzene, and 15 parts of dichloromethane was blended while stirring. Thereafter, the resulting composition was dip-coated onto said charge generating layer, whereby a 20 μ m thick charge transport layer was provided.

Subsequently, a mixture consisting of 30 weight parts of acryl based monomer having the structural formula described below,



50 weight parts of ultra fine tin oxide particles having an average particle diameter of 400 Å prior to dispersion, 20 weight parts of fine polytetrafluoroethylene resinous powder (having an average particle diameter of 0.18 μm), 18 weight parts of 2-methylthioxanthone as the photopolymerization initiator, and 150 weight parts of ethanol was dispersed employing a sand mill over 66 hours.

The resulting composition was dip-coated onto said charge transport layer so as to form a layer. The resulting layer was photo-hardened for 60 seconds under a light intensity of 800 W/cm² employing a high-pressure mercury arc, and subsequently dried at 120 °C for 2 hours by a hot airflow, whereby a surface layer was prepared. The thickness of the resulting surface layer was 3 μm.

(2) Examples B-2 and B-3

Present Photoreceptors B-2 and B-3 were prepared as described below.

An aluminum drum, a conductive layer, a sublayer, a charge generating layer, and a charge transport layer, which were the same as Example B-1, were prepared.

Subsequently, 30 weight parts of acryl based monomers, 50 weight parts of fine tin oxide particles, 2 weight parts of fine polytetrafluoroethylene resinous powder, 18 weight parts of a photopolymerization initiator, and 150 parts of ethanol, each of which were the same as Example B-1, were dispersed over 66 hours, employing a sand mill.

Further, separately, 30 weight parts of acryl based monomers, 50 weight parts of ultra fine tin oxide particles, 6 weight parts of fine polytetrafluoroethylene resinous powder, 18 weight parts of the photopolymerization initiator, and 150 weight parts of ethanol, each of which were the same as Example B-1, were dispersed employing a sand mill over 66 hours. Each of these compositions was coated onto said charge transport layer employing a dip coating method to form a layer under the same conditions as Example B-1, whereby a 3 μ m thick surface layer was prepared.

(3) Comparative Example

Comparative Example was prepared as described below.

A photoreceptor, wherein fine polytetrafluoroethylene resinous powder was not blended in the surface layer of Present Photoreceptor B-1, was designated as Comparative Photoreceptor.

[Contact Angle] The contact angle of photoreceptor drum surface to pure water was determined employing a dripping type contact angle meter, and subsequently compared. As a result, Example B-1 photoreceptor resulted in a large contact angle of 118 degrees and was subjected to achievement of a low energy surface. By contrast, said comparative photoreceptor resulted in a relatively small contact angle of 80 degrees, whereby a low energy surface was not achieved.

ii) Cleaning Roller

The cleaning roller was comprised of conductive foamed urethane, and was comprised of an elastic roller having a surface resistivity of $10^3 \Omega/\square$ and a hardness of 30 degrees. Said roller was prepared by winding urethane onto a $\Phi 6$ mm metal shaft so as to form $\Phi 16$ mm (being a thickness of 25 mm) and was brought into contact with said photoreceptor to result in a contact width of 2 mm.

Said roller moved in the normal direction to said photoreceptor in the contact area at a circumferential speed ratio of 1 : 1.

iii) Bias Voltage

A current at 20 μ A and a positive bias voltage were applied to said cleaning roller employing a constant current power source.

iv) Removal Means

A scraper made of SUS was brought into contact with said cleaning roller utilizing a counter system.

v) Cleaning Blade

A cleaning blade comprised of urethane rubber, having a thickness of 2.0 mm, a free length of 10 mm, and a hardness of 70 degrees, was brought into contact with said photoreceptor at a contact angle of 15 degrees, utilizing a counter system. The contact load was 20 g/cm.

vi) Developer

A two-component developer comprised of a toner and a carrier was employed. Said toner, having a volume average particle diameter of 6.5 μ m, was prepared employing a granulation polymerization method.

Image formation experiments, employing 200,000 sheets, were carried out under the conditions previously described and the ambient conditions described below. The following results were obtained.

- a. Normal temperature and normal humidity from the 1st to the 100,000th sheet (20 °C and 50 percent relative humidity)
- b. Low temperature and low humidity from the 100,001th to the 200,000th sheet (10 °C and 20 percent relative humidity)

It was confirmed that Examples B1 through B3 resulted in sufficient cleaning until the image formation of the 200,000th sheet and were capable of consistently outputting high quality images without image problems such as white streaks.

Comparative Example resulted in excellent images during the initial stage (until the 100,000th sheet). However, in the image formation after the 130,000th sheet, insufficient cleaning occurred due to excessive abrasive wear of the cleaning roller surface, whereby white streaks and black streaks were formed on the images. Said trend became more pronounced as the image formation proceeded. At the completion of the image formation of the 150,000th sheet, in order to continue the image formation, white streaks as well as black streaks were eliminated by increasing the current of the bias power to +55 μ A. However, acceptable images were not obtained due to discharge generation from the cleaning roller to the photoreceptor.

Example 4

Production of Toners T1 and T2 (Example of Emulsion Polymerization Method)

Added to 10.0 liters of deionized water was 0.90 kg of sodium n-dodecyl sulfate, which was dissolved while stirring. Gradually added to the resultant solution were 1.20 kg of Regal 330R (carbon black, manufactured by Cabot Co.), and stirred well for one hour. Thereafter, the resultant mixture was continuously dispersed for 20 hours, employing a sand grinder (a medium type homogenizer). The resultant dispersion was designated as "Colored Dispersion 1". Further, a solution comprised of 0.055 kg of sodium dodecylbenzenesulfonate and 4.0 liters of deionized water was designated as "Anionic Surface Active Agent Solution A".

A solution comprised of 0.014 kg of nonyl phenyl polyethylene oxide 10-mole addition product and 4.0 liters of deionized water was designated as "Nonionic Surface Active Solution B". A solution prepared by dissolving 223.8 g of potassium persulfate in 12.0 liters of deionized water was designated as "Initiator Solution C".

Placed into a 100-liter GL (glass lining) reaction tank, fitted with a thermal sensor, a cooling pipe, and a nitrogen gas introducing device, were 3.41 kg of wax emulsion

(polypropylene emulsion having a number average molecular weight of 3,000, a number average primary particle diameter of 120 nm, and a solid portion concentration of 29.9 percent), all of "Anionic Surface Active Agent Solution A", and all of "Nonionic Surface Active Agent B", and the resultant mixture was stirred. Subsequently, 44.0 liters of deionized water were added.

When the mixture was heated to 75 °C, all of "Initiator Solution C" was added dropwise. Thereafter, while maintaining the temperature of the mixture at 75 ± 1 °C, 12.1 kg of styrene, 2.88 kg of n-butyl acrylate, 1.04 kg of methacrylic acid, and 548 g of t-dodecylmercaptan were added dropwise. After finishing dropwise addition, the mixture was heated to 80 ± 1 °C and stirred for 6 hours while being heated. Subsequently the resultant mixture was cooled to not more than 40 °C, and stirring was terminated. Said mixture was filtered employing a pole filter and the resultant filtrate was designated as "Latex (1)-A".

Incidentally, the glass transition temperature of resinous particles in Latex (1)-A was 57 °C, and the softening point of the same was 121 °C. The molecular weight distribution of the same exhibited parameters such as a

weight average molecular weight of 12,700 and a weight average particle diameter of 120 nm.

Further, a solution, prepared by dissolving 0.055 kg of sodium dodecylbenzene sulfonate in 4.0 liters of deionized water, was designated as "Anionic Surface Active Agent Solution D". Still further, a solution prepared by dissolving 0.014 kg of nonyl phenol polyethylene oxide 10-mole added product in 4.0 liters of deionized water was designated as "Nonionic Surface Active Agent Solution E".

A solution, prepared by dissolving 200.7 g of potassium persulfate (manufactured by Kanto Kagaku Co.) in 12.0 liters of deionized water, was designated as "Initiator Solution F".

Placed into a 100-liter GL reaction tank, fitted with a thermal sensor, a cooling pipe, a nitrogen gas introducing device, and a comb-shaped baffle, were 3.41 kg of wax emulsion (polypropylene emulsion having a number average molecular weight of 3,000, a number average primary particle diameter of 120 nm, and a solid portion concentration of 29.9 percent), all of "Anionic Surface Active Agent Solution D", and all of "Nonionic Surface Active Agent E", and the resultant mixture was stirred. Subsequently, 44.0 liters of deionized water were added. When the mixture was heated to 70 °C, "Initiator Solution F" was added. Subsequently, a

solution previously prepared by mixing 11.0 kg of styrene, 4.00 kg of n-butyl acrylate, 1.04 kg of methacrylic acid, and 9.02 g of t-dodecylmercaptan was added dropwise. Thereafter, while maintaining the temperature of the mixture at 72 ± 2 °C, stirring was carried out for 6 hours while being heated. The temperature was further raised to 80 ± 2 °C, and stirring was carried out for 12 hours while being heated. The resultant solution was cooled to not more than 40 °C, and stirring was terminated. Filtration was carried out employing a pole filter, and the resultant filtrate was designated as "Latex (1)-B."

The glass transition temperature of resinous particles in Latex (1)-B was 58 °C, and the softening point of the same was 132 °C. The molecular weight distribution of the same exhibited parameters such as a weight average molecular weight of 245,000 and a weight average particle diameter of 110 nm.

A solution, prepared by dissolving 5.36 kg of sodium chloride as the salting-out agent in 20.0 liters of deionized water, was designated as "Sodium Chloride Solution G".

A solution, prepared by dissolving 1.00 g of a fluorine based nonionic surface active agent in 1.00 liter of

deionized water, was designated as "Nonionic Surface Active Agent Solution H".

Placed into a 100-liter SUS reaction tank, fitted with a thermal sensor, a cooling pipe, a nitrogen gas introducing device, and a particle diameter and shape monitoring device (a reaction apparatus in which the crossed axis angle α is set at 20 degrees) were 20.0 kg of Latex (1)-A and 5.2 kg of Latex (1)-B prepared as described above, 0.4 kg of colorant dispersion, and 20.0 kg of deionized water and the resultant mixture was stirred. Subsequently, said mixture was heated at 40 °C, which was added to Sodium Chloride Solution G, 6.00 kg of isopropanol (manufactured by Kanto Kagaku Co.) and Nonionic Surface Active Agent Solution H in said order. Thereafter, the mixture was set aside for 10 minutes and then heated to 85 °C over 60 minutes. At 85 ± 2 °C, the mixture was stirred from 0.5 to 3 hours, so that the particle diameter increased under salting-out/fusion. Subsequently, 2.1 liters of pure water was added, to terminate the increase in the particle diameter.

Placed into a 5-liter reaction vessel, fitted with a thermal sensor, a cooling pipe, and a particle diameter and shape monitoring device were 5.0 kg of the fused particle

dispersion prepared as described above, and the shape was controlled while stirring at the dispersion temperature of $85 \pm 2^\circ\text{C}$ from 0.5 to 15 hours. Thereafter, the resultant dispersion was cooled to not more than 40°C and stirring was terminated. Subsequently, classification was carried out in the suspension by a centrifugal sedimentation method employing a centrifuge, and the resultant mixture was filtered employing a $45\ \mu\text{m}$ opening sieve. The resultant filtrate was designated as Association Liquid (1). Subsequently, wet cake-like non-spherical particles were collected from said Association Liquid (1) through filtration, employing glass filter and then washed with deionized water.

The resultant non-spherical particles were dried employing a flash jet drier at an intake air temperature of 60°C , and subsequently dried at 60°C , employing a fluidized-bed dryer. Externally blended with 100 parts, by weight, of the obtained colored particles were one part by weight of fine silica particles and 0.1 part by weight of zinc stearate, employing a Henschel mixer, and thus toners shown in the table below were obtained which were prepared employing the emulsion polymerization association method.

Toner T1 and Toner T2 shown in Table 4-1 were obtained by controlling the stirring rotation rate and the heating time during monitoring of said salting-out/fusion stage as well as the shape controlling process, and further by adjusting the particle diameter and the variation coefficient of the grain size distribution.

Table 4-1

Toner No.	Ratio of Shape Coefficient of 1.0 to 1.6 (in percent)	Ratio of Shape Coefficient of 1.2 to 1.6 (in percent)	Variation Coefficient of Shape Coefficient (in percent)	Ratio of Toner Particles having no Coroners (in percent)
Toner 1	82.5	68.3	15.2	88
Toner 2	63.9	62.0	17.4	53

Toner No.	Number Average Particle Diameter (in μm)	Variation Coefficient of Number Distribution (in percent)	Sum M of m_1 and m_2 (in percent)
Toner 1	5.6	25.9	80.7
Toner 2	5.4	25.9	68.5

A ferrite carrier in an amount of 200.1 g having a volume average particle diameter of 45 μm , which had been coated with styrene-methacrylate resin, was blended with each of 19.8 g of said toners 1 and 2, and Developers for the evaluation were prepared.

On a cylindrical aluminum electrically conductive support an inter layer was provided, on which the organic light semiconductor layer was provided to prepare the photoreceptor for an photoreceptor. The organic light semiconductor layer was composed of a charge generation layer containing charge generation material, phthalocyanine pigment, having thickness of 0.5 μm , and a charge transfer layer formed by coating triphenyl amine based charge transfer material dissolved in polycarbonate resin having thickness of 25 μm .

(Image Forming Apparatus)

Aforesaid photoreceptor was installed in a digital copier, Konica 7033, manufactured by Konica Corp., which basically had the same structure as the image forming apparatus in Fig. 1(b). The charging potential of the image section and the potential in the maximum image density section were adjusted to -750 V and -100 V, respectively, and reversal development was carried out.

Further, said copier was modified and a set of two of each cleaning members prepared as described below was installed.

(Cleaning Member)

Cleaning Member A

Said member was a roller having a volume resistivity of $10^4 \Omega \cdot \text{cm}$, comprised of conductive foamed urethane, which was brought into contact with the photoreceptor. The circumferential speed ratio in the contact section was such that photoreceptor : roller = 1 : 1.1.

A scraper for removing recovered toner was installed, while electric current was not applied. The toner removal ratio on the surface of the photoreceptor was 55 percent.

Cleaning Member B

Said member was constituted in the same manner as Cleaning Member A, but electric current of $+10 \mu\text{A}$ was applied. The toner removal ratio on the surface of the photoreceptor was 75 percent.

Cleaning Member C

Said member was constituted in the same manner as Cleaning Member A, but an electric current of $+10 \mu\text{A}$ was applied. The toner removal ratio on the surface of the photoreceptor was 95 percent.

Cleaning Member D

Said member was a rayon brush roller.

Said member was brought into contact with the photoreceptor, and the circumferential speed ratio in the contact section was that of the photoreceptor : roller = 1 : 1.2.

A flicker bar for removing recovered toner was installed, while an electric current was not applied. The toner removal ratio on the surface of the photoreceptor was 30 percent.

Cleaning Member E

Said member was a urethane rubber blade, having a hardness of 70 degrees, a thickness of 2.0 mm and a free length of 10 mm.

Said blade was brought into contact with the photoreceptor so as to form a contact angle of 10 degrees to its surface. The contact load was set at 120 mN/cm. The toner removal ratio on the surface of the photoreceptor was 90 percent.

Cleaning Member F

The same conditions as Cleaning Member E were set except that the contact load was varied to 50 mN/cm. The toner removal ratio on the surface of the photoreceptor was 40 percent.

Properties Evaluation

At the combinations shown in Table 4-2 below, imaging tests employing 200,000 copy sheets were carried out.

The test to the 100,000th sheet was carried out at normal temperature and normal humidity (20 °C and 50 percent relative humidity), while from the 100,001st to the 150,000th sheet was a low temperature and low humidity (10 °C and 20 percent relative humidity), and from the 150,001st sheet, was a high temperature and high humidity (30 °C and 80 percent relative humidity).

Regarding evaluation items; insufficient cleaning (insufficient residual toner removal), image problems (white streaks and black streaks), the photoreceptor surface and copy images were visually observed.

Table 4-4-2

	First Cleaning Member	Second Cleaning Member	Toner	Insufficient Cleaning	Image White Streaks	Image Black Streaks	Remarks
Example 4-1	A(55%)	E(90%)	1	good to the 200,000th copy	none	none	
Example 4-2	C(95%)	E(90%)	1	good to the 200,000th copy	none	none	
Example 4-3	E(90%)	D(30%)	1	good to the 200,000th copy	none	none	
Example 4-4	B(75%)	A(55%)	1	good to the 200,000th copy	none	none	
Comparative Example 4-1	D(30%)	C(95%)	1	occurred at about the 120,000th copy	occurred at about the 140,000th copy	occurred at about the 120,000th copy	
Comparative Example 4-2	F(40%)	E(90%)	1	occurred at about the 140,000th copy	occurred at about the 150,000th copy	occurred at about the 140,000th copy	
Example 4-5	C(95%)	E(90%)	2	good to the 200,000th copy	slightly occurred at about the 150,000th copy	none	interior apparatus staining due to scattering, generation of white streaks due to stained charging pole

Figures in parentheses are the toner removal ratio.

In Examples 4-1 through 4-4, excellent images were obtained until the 200,000th copy. On the other hand, in Comparative Examples 4-1 and 4-2, image problems due to insufficient cleaning occurred and each test was suspended.

In Example 4-5, properties were slightly degraded compared to Example 4-1 through 4-4. The resulting degradation was assumed due to an increase in the range of charge amount caused by the extremely deformed toner particle shape.

According to the present invention, it is possible to provide an image forming apparatus and an image forming method which is capable of resulting in stable cleaning properties over an extended period of time and of forming high quality images without formation of image problems such as white streaks and black streaks.